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Acute Toxicity, Bioconcentration and Persistence of AC 222,705, Benthiocarb, Chlorpyrifos, Fenvalerate, Methyl Parathion and Permethrin in the Estuarine Environment

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16. ABSTRACT

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Acute Toxicity, Bioconcentration, and Persistence of AC 222,705, Benthiocarb, Chlorpyrifos, Fenvalerate, Methyl Parathion, and Permethrin in the Estuarine Environment

Steven C. Schimmel,*[1] Richard L. Garnas,[2] James M. Patrick, Jr., and James C. Moore

Six pesticides were evaluated in laboratory studies to determine acute (96-h) toxicity, octanol–water partition coefficient (log *P*), solubility, and persistence in seawater. In addition, three of the six pesticides (synthetic pyrethroids) were tested by using the eastern oyster (*Crassostrea virginica*) in long-term (28-day) tests to determine their respective bioconcentration factors (BCF). Acute toxicity tests provided the following decreasing order of toxicity to estuarine crustaceans and fishes: AC 222,705, fenvalerate, permethrin, chlorpyrifos, methyl parathion, and benthiocarb. The estuarine mysid (*Mysidopsis bahia*) was consistently the most sensitive species, with LC_{50} values as low as 0.008 μg/L. The sheepshead minnow (*Cyprinodon variegatus*) was generally the least sensitive (range of LC_{50} values = 1.1–1370 μg/L). log *P* values were inversely related to solubility in seawater. The following are the increasing order of log *P* values (range 1.8–6.5) and decreasing order of solubility (range >1000–24 μg/L): methyl parathion, benthiocarb, chlorpyrifos, AC 222,705, fenvalerate, and permethrin. Pesticide half-lives in sediment–water studies ranged from 1.2 to 34 days and were in the following order of increasing persistence: methyl parathion, permethrin, benthiocarb, AC 222,705, chlorpyrifos, and fenvalerate. The steady-state BCF's of the three synthetic pyrethroids were 1900 for permethrin, 2300 for AC 222,705 and 4700 for fenvalerate. After termination of the exposure, each insecticide was depurated by oysters to nondetectable concentrations within 1 week.

The manufacture and use of organochlorine pesticides in the United States have decreased in the last decade, in part due to their adverse effects on fish and wildlife and the tendency of these chemicals to bioconcentrate. Replacement of these pesticides in the agricultural industry fell initially on the organophosphate insecticides and, more recently, the synthetic pyrethroid insecticides. Chlorpyrifos [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate] and methyl parathion [*O,O*-dimethyl *O*-(4-nitrophenyl) phosphorothioate] (Figure 1) are organophosphate insecticides that have been in use for many years. Permethrin [3-phenoxybenzyl (±)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], fenvalerate [(*RS*)-α-cyano-3-phenoxybenzyl (*RS*)-2-(4-chlorophenyl)-3-methylbutyrate], and AC 222,705 [(*RS*)-α-cyano-3-phenoxybenzyl (*RS*)-2-[4-(difluoromethoxy)phenyl]-3-methylbutyrate] (Figure 1) are synthetic pyrethroid insecticides that were introduced during the 1970s (Miester, 1980) and are in wide use throughout western Europe and Japan. The registration of AC 222,705 (Payoff), permethrin, and fenvalerate by the U.S. Environmental Protection Agency (EPA) is limited essentially to cotton application. the herbicide benthiocarb [*S*-(4-chlorobenzyl) diethylthiocarbamate] (Figure 1) is now registered by EPA for use in rice fields to control weed growth.

Evaluation of the relative hazards of these chemicals to aquatic environments requires that information on toxicity, accumulation potential, and expected environmental concentrations be compared. We therefore initated a series of studies on these six pesticides to determine (1) the acute

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Table I. Sampling Schedules and Test Conditions for Conducting Eastern Oyster Bioconcentration Tests with Three Pyrethroid Insecticides

insecticide	sampling days: uptake	sampling days: depuration	temperature, °C [mean (range)]	salinity, °/₀₀ [mean (range)]
AC 222,705	0,[a] 1.75, 3.5, 7, 14, 21, 28	29.75, 31.5, 35, 38, 42, 48, 52	28.7 (24-31)	29.1 (18.5-32)
fenvalerate	0,[a] 1, 2, 5, 10, 20, 21, 23, 28	29, 33, 37	28.6 (26-30)	23.8 (17.5-28.5)
permethrin	0,[a] 2, 5, 9, 15, 20, 23, 31	33, 40	27.7 (22.5-30)	21.9 (17.5-29)

[a] Pretest sample.

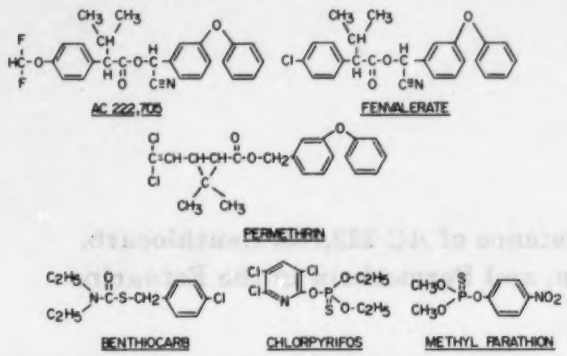

Figure 1. Chemical structures of pesticides examined in these studies.

toxicity of these pesticides to selected estuarine animals, (2) the logarithm of the octanol–water partition coefficient (log *P*) and solubility of these chemicals in seawater, (3) the persistence in various seawater–sediment conditions, and (4) the steady-state bioconcentration factors of synthetic pyrethroids in eastern oysters (*Crassostrea virginica*).

MATERIALS AND METHODS

Test Animals. All test animals, except the Atlantic silversides (*Menidia menidia*), used in the acute (96-h) lethality tests were either collected from estuarine waters adjacent to the Environmental Research Laboratory (ERL), Gulf Breeze, or cultured in the laboratory from laboratory stocks. The silversides were shipped as embryos to the laboratory by air express from Charleston, SC, and reared at the Gulf Breeze Laboratory. Mortality of animals was less than 1% in the 48 h preceding testing, and they exhibited no obvious diseases or abnormal behavior during acclimation. Fishes were acclimated to laboratory conditions at least 14 days prior to testing. For the mysid (*Mysidopsis bahia*) tests, newly hatched (≤24-h) individuals were used.

Eastern oysters (*Crassostrea virginica*) used in the AC 222,705, permethrin, and fenvalerate bioconcentration studies were collected from concrete pilings in an estuarine area near the laboratory. Oysters were held for at least 7 days prior to testing.

Acute Lethality Tests. Methods used in the acute lethality tests followed the flow-through procedures of the American Society for Testing and Materials (1980) except that brine shrimp (*Artemia* sp.) nauplii were fed to mysids and silversides to prevent starvation during the 96-h test period. Another deviation from the ASTM method was the use of 2 mL/L of solvent for a fenvalerate test with sheepshead minnows (0.5 mL/L is recommended). A higher solvent concentration was necessary due to the low solubility of the insecticide in seawater. The acute lethality of the pesticides AC 222,705, benthiocarb, chlorpyrifos, methyl parathion, fenvalerate, and permethrin was determined by exposing 20 animals per aquarium to each concentration for 96 h. Stock solutions of each pesticide, made by dissolving them in triethylene glycol (TEG), were metered by pumps at 20 mL/day into filtered seawater that entered each aquarium from siphons calibrated to deliver 360 L/day. One control aquarium for each test received the same quantity of seawater and TEG with no pesticide; the second received only seawater at 360 L/day. Mortality was recorded daily and dead animals were removed when discovered.

Toxicity tests with mysids, because of their small size, required several modifications in the above procedures. We placed five animals (≤24-h-old juveniles) in each of four replicate chambers (15 cm diameter × 10 cm high cylinder) in each test concentration, using the methods of Nimmo et al. (1978). Seawater delivery was provided by siphons calibrated to deliver 360 L/day.

Bioconcentration Tests. Long-term bioconcentration studies were conducted individually on AC 222,705, fenvalerate, and permethrin, with the eastern oyster (*Crassostrea virginica*). For each study, 65 oysters (>4 and <8 cm umbo to distal valve edge height) were placed in each 80-L test chamber that received unfiltered seawater from siphons calibrated to flow at the rate of 2400 L/day. One exposure concentration and a control were used for each test. Stock solutions were prepared by dissolving each insecticide in reagent-grade acetone. The solution was then placed in 50-mL syringes and injected by syringe pump at the rate of 20 mL/day. The control oysters received acetone at the rate of 20 mL/day. During the uptake portion of each test, four oysters were randomly sampled from the experimental aquaria on each sampling day (Table I) and analyzed individually. Duplicate water samples were taken and analyzed individually whenever oysters were removed for analysis. Four control oysters were sampled at days 0 (pretest sample) and 14 and at the end of the exposure period.

At the end of the exposure portion of each test, experimental oysters were removed from their exposure aquaria. The aquaria were cleaned and the oysters replaced in the aquaria and provided unfiltered seawater at the rate of 2400 L/day. Oysters were sampled (Table I) until pyrethroids were not detected in tissues for two successive sampling periods. Control oysters were sampled at the end of the depuration period.

Selection of nominal exposure concentrations of the insecticides was based on tests that identified a concentration that would not affect shell deposition. In this test (Butler and Lowe, 1978), 10 μg/L or greater of each insecticide did not decrease shell deposition of oysters relative to the controls. Therefore, an exposure concentration of 1.0 μg/L was selected for each insecticide in the bioconcentration studies to minimize the potential for adverse effects during the longer term studies.

Seawater temperature and salinity were monitored continuously throughout each bioconcentration test (Table I); pH and dissolved oxygen were monitored weekly.

Octanol–Water Partition Coefficient (log *P*). Stock solutions were prepared in 1-octanol (Fisher Certified, A-402) at 1.0 mg/mL for permethrin, fenvalerate, AC

222,705, and benthiocarb and at 0.25 mg/mL for chlorpyrifos and methyl parathion. A 50-mL aliquot of stock was added to 1500 mL of distilled water (Milli-R/Q water purifier, Millipore Corp.) in a 2-L separatory funnel. The contents were agitated for 2 min and allowed to separate overnight at 25 ± 1 °C. The aqueous phase was decanted into six 300-mL stainless steel bottles and centrifuged for 30 min at 20000*g* (25 ± 1 °C). Approximately 175 mL of water was withdrawn from midcolumn of each bottle by pipet, and pipet stem was wiped to remove droplets of water containing traces of excess octanol, and the water was discharged into a 2-L separatory funnel until a total of 1000 mL was collected. The water was extracted and analyzed according to the procedures described for water samples. The octanol phase was decanted into a 150 mm by 25 mm screw-top test tube and centrifuged for 30 min at 1600*g*. A sample of the octanol phase was diluted with petroleum ether and analyzed according to methods to be described. Each determination was duplicated.

Solubility. A 4-mL aliquot of a pesticide stock solution (1.0 mg/mL) in acetone was added to a 4-L amber glass solvent bottle fitted with a Teflon screw cap. The bottle was rotated on its side and simultaneously purged with a gentle stream of nitrogen gas, so that the chemical uniformly coated the inner glass walls. Three and one-half liters of filtered seawater (15 μm; 22 ‰) was added to the bottle, and the contents were agitated continuously on a Eberbach shaker (Model 6000) at room temperature (22 ± 2 °C). Aliquots were withdrawn by pipet, centrifuged at 20000*g* for 30 min, and sampled, extracted, and analyzed according to the procedures used for the aqueous phase of the log *P* determination. Samples were taken at 24, 48, and 96 h. Each determination was duplicated, with steady-state values reported.

Persistence. Sediment was collected from a salt marsh adjacent to Range Point, Santa Rosa Island, Escambia County, FL. The sediment was characterized by a high organic matter content (48%), high moisture content (83%), and relatively small particle size (57% <0.002 mm^2). Carrier-free seawater solutions were prepared for each pesticide at concentrations less than the determined solubility by using the procedures described previously for solubility tests. For indoor studies, a series of 150-mL Corex centrifuge bottles contained 10 g (wet weight) of sediment and 100 mL of a pesticide solution. Appropriate controls were prepared for analytical blanks and fortification purposes. Some containers were prepared with sediments pretreated with 0.5 mL of formalin/g for 24 h. Aliquots were plated on 15 ‰ Zobell's medium throughout the study to confirm sterility. Another set of bottles that contained only 100 mL of a pesticide–seawater solution were stoppered and aerated at 50 mL/min. Air exiting each bottle passed through a 6 cm by 0.5 cm i.d. column of Amberlite XAD-4 resin to trap vaporized pesticide. All indoor studies were incubated at 25 °C with 12 h photoperiod under white fluorescent lights. These bottles were agitated continuously at 100 rpm on a rotator table. For all outdoor studies, 100-mL aliquots of a pesticide–seawater solution were added to 250-mL Pyrex Erlenmeyer flasks fitted with ground glass stoppers. Half of the flasks were covered with aluminum foil, and all flasks were exposed outdoors to ambient sunlight and temperature, which varied in the flask from a high of 45 °C during the day to a low of 22 °C at night.

Containers were sampled on days 0, 4, 7, 14, and 28; sediment-containing bottles were sampled in duplicate and all others were single samples. Sediments were centrifuged for 30 min at 1600*g* and the water phase was decanted into a separatory funnel for extraction. The sediment phase and the water phase were analyzed separately according to methods to be described. Following decantation of water from indoor systems that contained no sediment, the glass bottle was repeatedly rinsed with acetone to remove sorbed residues for quantitation; the glassware of sediment-containing bottles was periodically rinsed separately with acetone. The contents of one bottle served as a blank, and the contents of a similar bottle, following phase separation, were fortified by the method of known addition with the respective pesticide.

Since these studies were conducted over a period of 1 year with different batches of sediment and seawater, a set of containers that contained methyl parathion was run simultaneously with each pesticide, except fenvalerate, which was rerun with AC 222,705.

Analytical Procedure. *Water.* One liter of seawater was extracted twice with 100-mL portions of petroleum ether (Burdick and Jackson Laboratories, Inc., Muskegon, MI) by shaking for 1 min in a 2-L separatory funnel. Proportional adjustments were made for seawater for sediment studies. The solvent phase was dried by passage through a funnel containing heat-treated (600 °C) glass wool and collected in a 250-mL Kuderna-Danish concentrator. The concentrator was fitted with a Synder column and the solvent was evaporated on a steem cabinet to about 20 mL, followed by concentration with a nitrogen evaporator at room temperature to not less than 2 mL. The lower limits of detection and recovery data for fortified samples are given in Table II.

Tissue. One to eight grams of tissue was weighed into a 150 mm by 25 mm screw-top test tube and homogenized 4 times with 5 mL of acetonitrile by using a Willems Polytron Model PT 20-ST (Brinkman Instruments, Westbury, NY). Following each homogenization, the test tube was centrifuged (1600*g*) and the liquid layer was decanted into a 120-mL oil sample bottle. Seventy-five milliliters of 2% (w/v) aqueous sodium sulfate and 10 mL of either petroleum ether (fenvalerate) or 1:1 (v/v) diethyl ether–petroleum ether (permethrin and AC 222,705) were added to the bottle; the contents were shaken for 1 min, and the layers were allowed to separate. The solvent layer was transferred by pipet into a 25-mL concentrator tube, and the extraction procedure was repeated 2 more times. The combined solvent extract was concentrated to 1 mL on a nitrogen evaporator in preparation for cleanup.

Sediment. Ten grams of sediment (wet weight) contained in a 150-mL Corex bottle was homogenized 4 times with 25 mL of acetonitrile by using a Willems Polytron. Following each homogenization, the bottle was centrifuged (1600*g*) and the liquid was decanted into a 2-L separatory funnel. One liter of 22 ‰ filtered (15 μm) seawater was added to the funnel, and the contents were extracted and concentrated similarly to the procedure used for water samples.

Cleanup. Columns were prepared by adding 3 g of PR-grade Florisil (stored at 130 °C), followed by 2 g of anhydrous sodium sulfate (powder), to a 200 mm by 9 mm i.d. Chromaflex column (Kontes Glass Co., Vineland, NJ) and rinsing with 20 mL of hexane. Tissue and sediment concentrates were transferred with two additional 2-mL volumes of hexane to the column. Benthiocarb was eluted with 20 mL of 5% (v/v) diethyl ether in hexane; chlorpyrifos, with 20 mL of 10% (v/v) diethyl ether in hexane. Methyl parathion, fenvalerate, AC 222,705 and permethrin were eluted with 20 mL of 10% 2-propanol in isooctane, following a 20-mL rinse with 5% diethyl ether in hexane to removed chlorinated pesticides and PCB's. The lower

Table II. Pesticide Sources, Purities, Recoveries,[a] and Limits of Detection

parameter	permethrin	fenvalerate	AC 222,705	benthiocarb	methyl parathion	chlorpyrifos
technical material source	ICI Americas, Inc.	Shell Development Co.	American Cyanamid Co.	Chevron Chemical Co.	Chem Service Inc.	Dow Chemical Co.
purity, %	93	98	77	90	99	92
GC–MS base peak, *m/e*	184	125	199	100	109	97
GC–MS molecular ion, *m/e*	391	420	451	258	263	351
analytical standard, ng/L	0.50	0.30	0.30	1.0	0.10	0.03
water recovery, %	94	95	97	96	95	96
tissue recovery, %	97	92	88			
sediment recovery, %	82	88	91	88	90	95
lower limit of detection[b]	0.25	0.15	0.15	0.50	0.05	0.015

[a] $N > 12$; relative standard deviation < 9.6%. [b] ng/μL for 1 L of seawater; 1 g of sediment (dry weight) and 5 g of tissue (wet weight).

limits of detection and recovery data for fortified samples are given in Table II.

Resin. XAD-4 resin traps were eluted with 5 mL of acetone, which was concentrated to minimal volume with a nitrogen evaporator, and diluted to an appropriate volume with petroleum ether.

Analytical Equipment. Fenvalerate, AC 222,705 and permethrin analyses were performed on a Hewlett-Packard Model 5710 gas chromatograph equipped with a ^{63}Ni electron-capture detector. The column was 182 cm by 2 mm i.d. glass, packed with 3% OV-1 (Supelco, Inc., Bellefonte, PA) on 80–100-mesh Supelcoport. For fenvalerate and AC 222,705, the flow rate of the 10% methane in argon carrier gas was 25 mL/min, the column temperature 250 °C, the inlet temperature 200 °C, and the detector temperature 300 °C. Under these conditions, enantiomeric pairs were not separated completely. Conditions were similar for permethrin, with the exception that the column temperature was 225 °C; separation of the steroisomers was not complete.

Methyl parathion, chlorpyrifos, and benthiocarb analyses were performed with a Hewlett-Packard Model 5730A gas chromatograph equipped with a dual nitrogen–phosphorus flame ionization detector. Detector gases were hydrogen at 4 mL/min and air at 100 mL/min. Operating conditions were flow rate of helium carrier gas 30 mL/min, injector and column temperature 200 °C, and detector temperature 300 °C. The column was 182 cm by 2 mm i.d. glass, packed with 5% QF-1 on 80–100-mesh Gas-Chrom Q.

All chemicals were quantitated by peak area, with Hewlett Packard Model 3353E laboratory data system. Aliquots of 5 μL were injected and compared to the analytical standard concentrations noted in Table II. Tissue concentrations were calculated by wet weight; sediment concentrations, by dry weight.

Gas chromatography–mass spectrometry (GC–MS) data were obtained with a Finnigan Model 4000 EI-CI mass spectrometer interfaced to a System Industries System 150 data system. Spectra were determined at 70 eV in the electron impact (EI) model by using (decafluorotriphenyl)phosphine as the reference compound for calibration purposes (Eichelberger et al., 1975). The base peak and molecular ion were obtained for each chemical in the EI mode (Table II) and confirmed by further analysis in the chemical ionization (CI) mode. Columns were those mentioned for gas chromatographic analyses of each chemical.

Statistical Methods. Shrimp and fish acute lethality test data were analyzed by the probit analysis method of Finney (1971), moving average method (Kendall and Stuart, 1973), or the binomial test method (Siegal, 1956; Sokal and Rohlf, 1969) to determine the concentration of pesticide in water estimated to kill 50% of the test animals (LC_{50}) and the 95% confidence intervals (>99% for the binomial test method). Abbott's correction (Finney, 1971) was used to correct for control mortality (≤5% for fishes; ≤10% for shrimp) when observed.

In the bioconcentration studies, the statistical model of Bahner and Oglesby (1979) was used to determine bioconcentration factors and to describe uptake and depuration of AC 222,705 fenvalerate, and permethrin in oysters.

Each set of experimental data for the persistence studies was treated by linear regression under the assumption that pesticide concentration was first order with respect to time. The quality of the estimated regression lines was tested by determining the correlation coefficient and an analysis

Table III. Acute Toxicity of Six Pesticides to Estuarine Animals in Flowing Seawater Acute (96-h) Lethality Tests

pesticide	species	96-h LC_{50}, μg/L[a] (95% CI)	test temp (x), °C	test salinity
AC 222,705	*Mysidopsis bahia*, estuarine mysid	0.008[b] (0.006–0.01)	26.0	19.5
	Penaeus duorarum, pink shrimp	0.22 (0.15–0.70)	25.1	24.2
	Cyprinodon variegatus, sheepshead minnow	1.1 (0.38–1.3)	29.4	20.0
benthiocarb	*M. bahia*	330 (260–410)	27.6	25.5
	C. variegatus	1370 (1350–1380)	25.6	25.5
chlorpyrifos	*M. bahia*	0.035 (0.029–0.043)	26.8	26.7
	C. variegatus	136 (113–153)	31.4	10.3
	Fundulus similis, longnose killifish	4.1 (2.8–6.9)	30.0	25.9
	Menidia menidia, Atlantic silverside	1.7 (1.4–2.0)	27.5	24.3
	Mugil cephalus, striped mullet	5.4 (4.0–6.9)	24.8	24.7
fenvalerate	*M. bahia*, estuarine mysid	0.008[b] (0.005–0.01)	25.4	25.3
	P. duorarum, pink shrimp	0.84 (0.66–1.2)	24.8	24.9
	C. variegatus, sheepshead minnow	5.0 (4.8–5.3)	30.0	26.5
	M. menidia, Atlantic silversides	0.31 (0.21–0.40)	24.1	25.0
	M. cephalus, striped mullet	0.58 (0.41–1.0)	25.9	25.8
	Opsanus beta, Gulf toadfish	5.4 (4.6–6.6)	30.0	24.8
methyl parathion	*M. bahia*	0.78 (0.58–1.1)	19.5	14.0
	P. duorarum	1.2 (0.91–1.4)	24.8	21.6
permethrin	*M. bahia*	0.02[b] (0.017–0.024)	26.0	22.6
	P. duorarum	0.22 (0.06–0.79)	24.9	25.0
	C. variegatus	7.8 (6.2–10)	30.0	22.1
	M. menidia	2.2 (1.2–6.4)	25.5	25.0
	M. cephalus	5.5 (4.1–7.4)	24.5	19.0

[a] LC_{50} values based on measured concentrations. [b] LC_{50} values based on nominal concentrations.

of variance. The time to half concentration was computed from the regression equation, with corresponding 95% confidence intervals.

RESULTS

Acute Lethality. AC 222,705 and fenvalerate were the most toxic of the six pesticides tested (Table III). In general, our studies show the following decreasing order of toxicity: AC 222,705, fenvalerate, permethrin, chlorpyrifos, methyl parathion, and benthiocarb. As a group, the synthetic pyrethroids were toxic to all species tested at concentrations ≤7.8 μg/L. Benthiocarb, the only herbicide tested, was significantly less toxic than the five insecticides; methyl parathion, the second least toxic pesticide, was 423 times more toxic to mysid shrimp (*Mysidopsis bahia*) than benthiocarb.

Mysid shrimp were consistently the most sensitive species to all six pesticides, and sheepshead minnows were generally the least sensitive (Table III). Pyrethroid LC_{50} values for mysid shrimp were at least one-tenth those for another crustacean, *Penaeus duorarum*.

log *P*, Solubility, and BCF. The log *P* values for these six pesticides varied over 4 orders of magnitude (Table IV). The pyrethroids displayed the greatest affinity for the octanol phase, with a value of 6.2 for AC 222,705 and fenvalerate; the highest log *P* value in the study was 6.5 for permethrin. The two organophosphate insecticides differed markedly in log *P* values, with chlorpyrifos having the higher (log $P = 5.2$) and methyl parathion having the lowest of all six pesticides (log $P = 1.8$). The herbicide, benthiocarb, and a log *P* value of 3.4.

As expected, the solubility of the six pesticides in seawater was inversely related to the log *P* values (Table IV). The more hydrophobic insecticides, namely chlorpyrifos, AC 222,705, fenvalerate, and permethrin, had the lower solubilities, 73, 49, 24, and 50 μg/L, respectively. As a group the synthetic pyrethroids were very hydrphobic and extremely insoluble in seawater. Both methyl parathion and benthiocarb were less hydrophobic (Table IV) and more soluble in seawater than the highest value tested, 1000 μg/L.

Eastern oysters (*Crassostrea virginica*) accumulated all three synthetic pyrethroids in their tissues to concentrations exceeding 1900 times the concentration measured in the exposure water (Figure 2). Fenvalerate was accumulated the most with a steady-state bioconcentration factor (BCF; concentration of the insecticide measured in tissues at steady-state divided by the concentration of the insecticide measured in the exposure water) of 4700 (Table IV). The steady-state BCF for AC 222,705 was 2300 and that for permethrin, 1900. Steady-state was achieved in 15 days for fenvalerate, 7.7 days for the AC 222,705 test, and 2.5 days for permethrin. In pesticide-free water, oysters depurated permethrin and fenvalerate from tissues to nondetectable concentrations within 1 week; AC 222,705 was not detected in tissues after approximately 10 days (Figure 2).

Table IV. Octanol-Water Partition Coefficient[a] (log *P*), Solubility[b] (μg/L), and Steady-State Bioconcentration Factor[c] (BCF)

pesticide	log *P*	solubility	BCF
methyl parathion	1.8	>1000	
benthiocarb	3.4	>1000	
chlorpyrifos	5.2	73	
AC 222,705	6.2	49	2300
fenvalerate	6.2	24	4700
permethrin	6.5	50	1900

[a] log (concentration of pesticide in octanol/concentration of pesticide in water). [b] In seawater. [c] Concentration of pesticide in tissue at steady state/average concentration of pesticide in water.

Persistence. An assumption of first-order disappearance kinetics was used to determine the regression of the logarithm of pesticide concentration on sampling time for untreated estuarine sediment–water studies (Table V). With the exception of permethrin, an analysis of variance was performed for each regression. In each case, the null hypothesis was rejected at the $\alpha = 0.01$ level of significance, indicating that the assumption of first-order kinetics was valid. The half-lives and corresponding 95% confidence intervals, as determined from each regression, are reported in Table V. Methyl parathion had the lowest half-life of 1.2 (0.60–2.0) days. Half-lives of methyl parathion in identical studies run consecutively with each pesticide study over a period of 1 year did not exceed the 95%

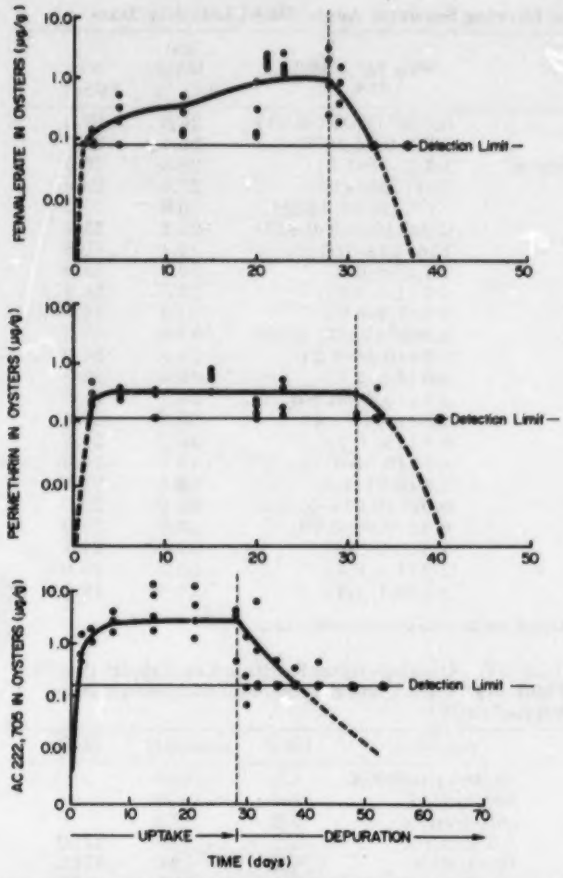

Figure 2. Uptake and depuration of AC 22,705, fenvalerate, and permethrin by eastern oysters (*Crassostrea virginica*) in flowing seawater tests.

Table V. Persistence Studies: Regression[a] of Pesticide Concentration on Sampling Time in Sediment Studies[b]

pesticide	N	b	a	r^2	half-life, days	95% CI[d]
methyl parathion[c]	12	−0.30	0.78	0.94	1.2	0.60–2.0
benthiocarb[c]	8	−0.048	0.90	0.85	6.4	4.0–9.0
chlorpyrifos[c]	10	−0.013	0.81	0.91	24	20–29
AC 222,705[c]	10	−0.019	0.61	0.88	16	13–21
fenvalerate[c]	9	−0.014	−0.22	0.87	34	27–42
	5	−0.011	0.43	0.94	27	20–35
permethrin					<2.5	

[a] $\bar{y} = a + bx$; $\bar{y}$ = log concentration; x = time. [b] Ten grams of sediment and 100 mL of a pesticide–seawater solution. [c] Analysis of variance performed for assumption of first-order disappearance; the null hypothesis was rejected at the $\alpha = 0.01$ level of significance. [d] 95% confidence interval.

confidence interval reported here. Chlorpyrifos was the more persistent of the two organophosphates examined, with a half-life of 24 (20–29) days. Benthiocarb, the only herbicide tested, and a half-life of 6.4 (4.0–9.0) days.

Fenvalerate was the most persistent pesticide in these studies, with a half-life of 34 (27–42) days. A duplicate study conducted over 1 year later gave remarkably similar results, 27 (20–35) days. Although sufficient data were not collected to compute a statistically significant regression, permethrin had the lowest half-life of all three pyrethroids, 2.5 days. The half-life and 95% confidence interval for

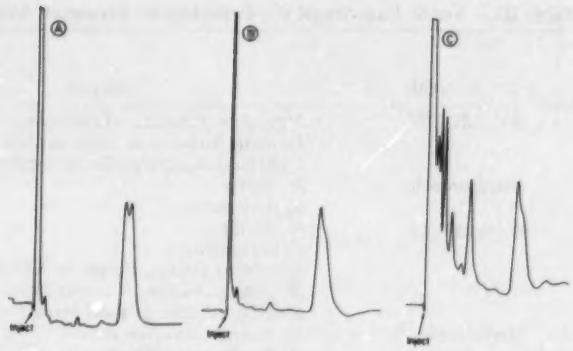

Figure 3. Gas chromatograms of extracts from studies with AC 222,705. (A) AC 222,705 standard response. (B) Tissue extract from the oyster bioconcentration study. (C) Sediment extract from the persistence study.

AC 222,705 was 16 (13–21) days. In this study and in the oyster bioconcentration test, AC 222,705 displayed selective loss of enantiomers, as is evident from the gas chromatograms in Figure 3. The response of the standard (A) with an electron capture detector is a doublet; analysis of tissue extract from an exposed oyster (B) and sediment extract from this persistence study (C) shows selective loss of the second peak of the doublet. Numerous controls, fortifications, and reinjections diminish the possibility that this observation is the result of an analytical artifact. This phenomenon did not occur for any other persistence test conditions with AC 222,705 or for the other two pyrethroids.

In other persistence studies, pesticide half-lives were determined by using a variety of experimental conditions (Table VI). Pretreatment of sediment-containing systems with formalin (sterile) resulted in no appreciable loss of any pesticide after 28 days and emphasized the importance of biological activity for pesticide half-life. In controlled laboratory conditions (indoor), the majority of the pesticides tested disappeared slowly from seawater solutions, the exceptions being benthiocarb and chlorpyrifos, which volatilized from the seawater. The resin traps accounted for 63% of the starting material in the chlorpyrifos studies and 45% in the benthiocarb studies. In contrast, these two pesticides failed to volatilize from sediment-containing system, as is evident from the half-lives for sterile tests. Pesticide half-lives were lower in outdoor seawater solution exposures. For the pyrethroids, the approximate half-lives for permethrin, fenvalerate, and AC 222,705 were 14, 8.0, and 6.1 days, respectively, as a result of sunlight exposure (outdoor—light), since little change in pesticide concentration occurred in foil-covered thermal controls (outdoor—dark). The two organophosphates, chlorpyrifos and methyl parathion, had half-lives of 4.6 and 6.3 days, respectively, from exposure to sunlight, with some loss of pesticide attributed to thermal decomposition. Within experimental error, benthiocarb failed to disappear in outdoor studies; it did not volatilize, as in indoor tests with seawater solutions, because flasks were stoppered.

DISCUSSION

AC 222,705, Fenvalerate, and Permethrin. A review of the literature revealed no data on the acute toxicity of AC 222,705 to fishes or aquatic invertebrates; however, the acute effects of fenvalerate and permethrin have been documented. Jolly and Avault (1978), Muirhead-Thompson (1978), Mulla et al. (1978), and Zitko et al. (1979) reported LC_{50} values 2–3 orders of magnitude higher than those we report for the mysid shrimp. Reasons for

Table VI. Persistence Studies: Pesticide Half-Lives for Different Experimental Conditions[a]

	half-life, days				
	sediment[b]		water[c]		
pesticide	untreated	sterile[d]	indoor[e]	outdoor—light[f]	outdoor—dark[g]
methyl parathion	1.2	>28[h]	>28[h]	6.3	18
benthiocarb	6.4	>28[h]	8.7[i]	>14[h]	>14[h]
chlorpyrifos	24	>28[h]	<2.0[i]	4.6	7.1
AC 222,705	16	>28[h]	26	6.1	38
fenvalerate	34	>28[h]	>28[h]	8.0	>14[h]
permethrin	<2.5	>28[h]	>21[h]	14	>14[h]

[a] Except for untreated sediment–water studies, sufficient numbers of samples were not analyzed for statistical validation. [b] Ten grams of sediment and 100 mL of a pesticide–seawater solution. [c] One hundred milliliters of pesticide–seawater solution. [d] One-half of milliliter of formalin/gram of sediment. [e] 25 °C with 12-h photoperiod white fluorescent light. [f] Stoppered, Pyrex flasks exposed to ambient sunlight and temperature (22–45 °C). [g] Foil-covered flasks. [h] Within experimental error, no significant change in pesticide concentration. [i] Pesticide volatilized, as determined by analysis of XAD resin traps.

Table VII. Comparative Acute Toxicity of Four Classes of Pesticides Tested at the Environmental Research Laboratory, Gulf Breeze, 1960–1980.

pesticide class (no. pesticides tested) [no. species tested]	most sensitive species	most toxic pesticide	96-h LC_{50}, μg/L	reference
organochlorine (>24) [>3]	*Panaeus duorarum*, pink shrimp	analytical-grade heptachlor	0.03	Schimmel et al. (1976)
organophosphate (>26) [>3]	*P. duorarum*	baytex (Bayer 29493)	0.060[a]	Butler (1963)
carbamate (>10) [>3]	*Penaeus aztecus*, brown shrimp	carbaryl	2.5[a]	Butler (1963)
synthetic pyrethroid (3) [4]	*Mysidopsis bahia*, mysid shrimp	AC 222,705 and fenvalerate	0.008	present study

[a] 48-h EC_{50}.

the disparity may be due to the sensitivity of the mysid shrimp compared to the species they tested, but differences in test procedures (static vs. flow through) or in shorter duration of exposure in some tests (Muirhead-Thompson, 1978) may account for the higher LC_{50} values reported in the literature.

The 96-h LC_{50} values for AC 222,705 and fenvalerate to mysids were the lowest (i.e., most toxic) of any chemicals tested at the Gulf Breeze Laboratory over the past 20 years (Table VII). On the basis of mysid sensitivity to the three pyrethroids at concentrations at least 1 order of magnitude lower than those detectable by chemical analysis (Table II), any detection of these insecticides in estuarine waters would likely be associated with adverse effects on the biotic component of that system.

Although no reports are available in the literature regarding the acute toxicity of AC 222,705 to fishes, the acute effects of fenvalerate on fish in static tests have been documented by Mulla et al. (1978) and Coats and O'Donnell-Jeffery (1979), whose reported LC_{50} values (3.0–200 μg/L) are generally higher than ours (0.31–5.0 μg/L) and may be due to differences in exposure conditions (static vs. flow-through tests) and test duration (24–48-vs. 96-h exposures). These authors also included acute static test values for five fish species exposed to permethrin that ranged from 5 to 135 μg/L (fish LC_{50} values in this study ranged from 2.2 to 7.8 μg/L). In 96-h flowing toxicity tests with permethrin, LC_{50} values for seven freshwater fish species (*Salmo gairdneri*, *Carassius auratus*, *Cyprinus carpio*, *Pimephales promelas*, *Ictalurus melas*, *Ictalurus punctatus*, and *Lepomis macrochirus*) ranged from 1.58 to 14.2 μg/L (Meyer, 1980).

Although water solubilities reported elsewhere for synthetic pyrethroids, including permethrin and fenvalerate (Coats and O'Donnell-Jeffery, 1979; Zitko et al., 1979), are similar to ours, published partition coefficients are at least 2 orders of magnitude lower than ours. Problems associated with the determination of partition coefficients have been addressed by Karickhoff and Brown (1979). At their suggestion, we also used an alternative method to estimate partition coefficients, namely, relative retention time with high-pressure liquid chromatography. Using the method of Veith et al. (1979a), we obtained partition coefficients within 0.5 order of magnitude of those we reported for octanol–water partition.

The bioconcentration factors of pyrethroids in eastern oysters are also larger than values reported by others. The bioconcentration of the (*S*)-acid isomer of fenvalerate by carp in a 24-h renewal exposure after 7 days of exposure to [^{14}C]fenvalerate was approximately 1100 (Ohkawa et al., 1980). After 7 days of depuration in toxicant-free water, 75% of the ^{14}C activity in tissue was lost. In a 30-day experiment also using [^{14}C]fenvalerate in an aquatic model ecosystem, bioaccumulation ratios were 100 for fish, 491 for snails, 303 for *Daphnia*, and 412 for algae. The authors concluded that metabolism by the biota, especially fish, was responsible for the low accumulated residues. At the Gulf Breeze Laboratory, 28-day chronic toxicity tests with *Cyprinodon variegatus* gave similar bioconcentration factors: 480 for permethrin, and 570 for fenvalerate (Hansen, 1981). Calculated steady-state bioconcentration factors for the synthetic pyrethroids, using the octanol–water partition coefficients and the regression equation of Veith et al. (1979b), are at least 1 order of magnitude higher than our values. The enzymatic metabolism of synthetic pyrethroids (Chambers, 1980) offers an explanation for this paradox.

The half-lives of all six pesticides are reported with those of other pesticides studied in our laboratory in Table VIII for untreated sediment–water studies. With the exception of kepone (half-life >90 days), fenvalerate had the highest half-life (34 days), followed by chlorpyrifos (24 days) and AC 222,705 (16 days). Chlorpyrifos and benthiocarb had the highest half-lives, respectively, of the organophosphates and carbamates.

Data from our persistence studies and data of others suggest that microbial activity may be a major factor in the disappearance of these pesticides. The addition of formalin, a typical biological sterilant, to our sediment studies inhibited loss of the pyrethroids. Other reports

Table VIII. Persistence Studies: Approximate Half-Lives for Different Pesticides Tested in 10 g of Sediment and 100 mL of Pesticide–Seawater Solution

pesticide	half-life, days
organochlorine	
pentachlorophenol	<2.0
kepone	>90
organophosphate	
phorate	<0.5
methyl parathion	1.2
EPN	2.3
carbophenothion	6.5
chlorpyrifos	24
carbamate	
carbaryl	1.7
diflubenzuron	<4.0
benthiocarb	6.4
pyrethroid	
permethrin	<2.5
AC 222,705	16
fenvalerate	34

offer additional support. Permethrin half-life in soil was approximately 28 days and was mediated by microbial metabolism, with degradation of the trans isomer occurring more rapidly than that of the cis isomer (Kaufman et al., 1977). The estimated half-life of permethrin and fenvalerate (WL 43775) in a variety of soils ranged from 3 to 4 weeks for permethrin, again with enhanced loss of trans isomer, and from 6 to 8 weeks for fenvalerate (Williams and Brown, 1979). Both high organic (52%) Cloverdale soil and sterilized soils displayed little loss of either pyrethroid after 16 weeks. Hill (1981) reported average half-lives for fenvalerate of 6.0 weeks in the field and 5.2 weeks when incubated indoors for Lethbridge soil, faster degradation being noted for the *RS,SR* enantiomeric pair. Our half-life values for permethrin (<2.5 days) and fenvalerate (34 days) are considerably less. Although the rapid degradation of permethrin did not allow examination of cis/trans isomer differences, selective degradation of AC 222,705 enantiomeric pairs was evident both in bioconcentration tests and in persistence studies and should be noted by others addressing environmental monitoring for AC 222,705 residues. Altogether, we reported three different sets of values that depend on biotransformation, namely, time to steady-state BCF, steady-state BCF, and half-life in sediment; each set ranks the three synthetic pyrethroids in the same order, i.e., fenvalerate > AC 222,705 > permethrin.

The quantitative expression of biotransformation rates has been suggested before by others (Baughman et al., 1980). Our correlations with first-order rates support their kinetic approach and contention that biotransformation studies should incorporate statistical treatment of data and mathematical analysis according to some proposed rate equations.

AC 222,705, fenvalerate, and permethrin did not disappear from seawater solutions in our studies unless exposed to ambient sunlight. Other investigations have also examined the photolysis of pyrethroids. Holmstead et al. (1978a,b) investigated the photochemical reactions of permethrin and fenvalerate and proposed pathways to account for the various photoproducts obtained in UV and sunlight studies, finding that the rate of disappearance was independent of solvent polarity; i.e., photolysis rates in hexane or water were similar. Ware et al. (1980) examined dislodgeable insecticide residues on cotton foliage for eight pesticides. If the reported data are treated with first-order kinetics, the calculated half-lives for AC 222,705, fenvalerate, and permethrin were 5.5, 6.3, and 3.0 days, respectively. Mikami et al. (1980) studied the photodegradation of fenvalerate in various natural waters, including seawater, and noted a lack of photosensitization. The photolysis half-lives we report are comparable to those cited. However, the synthetic pyrethroids are extremely hydrophobic and in aquatic environment will quickly become associated with organic bottom materials or suspended sediments. While we have demonstrated the importance of biotransformation reactions relative to sediments, it is doubtful that the photoreactivity of pyrethroids on sediments is a significant dissipation process environmentally, due to sunlight attenuation and scattering, although other investigations arrived at a different interpretation (Miller and Zepp, 1979).

In summary, our studies with the pyrethroid insecticides show that they are extremely toxic to estuarine animals. Estuarine invertebrates are particularly sensitive; 96-h LC_{50} values for two insecticides were <10 ng/L. In addition, they are bioconcentrated from water by oysters from 1900 to 4700 times, and their half-lives in sediment–seawater systems ranged from <2.5 days (permethrin) to 34 days (fenvalerate). Our results thus indicate that if synthetic pyrethroids are used in areas adjacent to estuarine systems, they may represent a substantial threat in their acute toxicity (at concentrations $^1/_{20}$ of those detectable by our analytical methods), their tendency to bioconcentrate in estuarine biota, and (for fenvalerate and AC 222,705) their tendency to persist in estuarine sediments.

Benthiocarb, Chlorpyrifos, and Methyl Parathion. Benthiocarb was acutely toxic to the freshwater fishes, *Salmo gairdneri*, *Lepomis macrochirus*, and *Ictalurus punctatus* with 96-h LC_{50} values ranging from 1.2 to 2.5 mg/L (Johnson and Finley, 1980). If the relationship of LC_{50} values for freshwater fishes to those for freshwater invertebrates is similar to those we found for estuarine species, we should expect enhanced sensitivity (lower LC_{50} values) for the freshwater invertebrate species. Proposed label instructions for benthiocarb providing recommended application rates for use on flooded rice fields (4 lb/acre, or 2.95 mg/L in 6 in. of water) indicate that aquatic animals in these fields would probably be adversely affected.

A substantial aquatic toxicity data base for the pesticide chlorpyrifos exists in the literature. In studies using saltwater fish species, Korn and Earnest (1974) reported a 96-h LC_{50} of 0.58 μg/L for striped bass (*Morone saxatilis*). Flow-through toxicity tests with three estuarine fishes (*C. variegatus*, *Fundulus similis*, and *Leiostomus xanthurus*) produced 48-h EC_{50} values of 1000, 3.2, and 7.0 μg/L, respectively (Lowe, 1980). Lowe's values for *F. similis* and *C. variegatus* are even more widely separated than those generated in this study. Lowe's chlorpyrifos studies on the invertebrate species, *Callinectes sapidus*, *Palaemonetes pugio*, *Penaeus duorarum*, and *Penaeus aztecus*, produced 48-h LC_{50} values that ranged from 0.2 to 5.2 μg/L. Chlorpyrifos toxicity may be directly related to temperature. Normally, the two penaeid shrimp species are very similar in sensitivity to pesticides. When Lowe exposed the two species to chlorpyrifos at temperatures that differed by 17 °C, *P. aztecus* exposed at 29 °C had an EC_{50} value of 0.2 μg/L; *P. duorarum* at 12 °C, 2.4 μg/L. Macek et al. (1969) reported the same temperature–toxicity relationship with rainbow trout (*Salmo gairdneri*) exposed to chlorpyrifos at 1.6, 7.2, and 12.7 °C.

Studies on chlorpyrifos with freshwater species generally compare favorably with those we report here. For example, the 96-h LC_{50} values for three species of stoneflies (*Pteronarcys californica*, *Pteronarcella badia*, and *Claassenia sabulosa*) were 10.0, 0.38, and 0.57 μg/L, respectively

(Sanders and Cope, 1968). Rainbow trout exposed to the insecticide for 96 h at three different temperatures gave LC_{50} values from 7.1 to 51 μg/L (Macek et al., 1969).

The acute toxicity of methyl parathion to the two crustaceans we report here (0.78 μg/L for *Mysidopsis bahia* and 1.2 μg/L for *P. duorarum*; Table III) compare favorably with those reported by others. Those for two populations of *P. aztecus* were 2.4 and 3.4 μg/L (Albaugh, 1972). Naqvi and Ferguson (1970) reported 24-h LC_{50} values ranging from 2.5 to 23.3 μg/L for four populations of the freshwater shrimp, *Palaemonetes kadiakensis*. Eisler (1969) reported 96-h LC_{50} values that ranged from 2 to 7 μg/L for the saltwater crustaceans, *Crangon septemspinosa*, *Palaemonetes vulgaris*, and *Pagurus longicarpus*. Muncy and Oliver (1963) reported a substantially higher 48-h LC_{50} value for the crayfish, *Procambarus clarki* (40 μg/L).

We could find no published reports of the solubility or octanol–water partition coefficient for benthiocarb. However, two related thiolcarbamate herbicides, EPTC (Cliath et al., 1980) and molinate (Soderquist et al., 1977), have reported solubilities that exceed 100 mg/L. Chlorpyrifos is soluble to 0.4 mg/L and its octanol–water partition coefficient is 5.11 (Chiou et al., 1977). Although we found no reported solubility or partition coefficient values for methyl parathion, ethyl parathion is soluble to 24 mg/L in distilled water and its partition coefficient is 3.81 (Chiou et al., 1977). These data are consistent with those we report.

If our chlorpyrifos partition coefficient is applied to the regression equation of Veith et al. (1979b) that estimates bioconcentration in fathead minnows, our calculated BCF is 5200. Although we did not determine the BCF for chlorpyrifos, Hansen (1981) reported BCF values of 1200 for *C. variegatus* and <400 for *Menidia menidia* in 28-day early life stage toxicity tests. Discrepanices between calculated and observed values may be the result of metabolism of chlorpyrifos by fish (Smith et al., 1966). Bioconcentration factors for methyl parathion and benthiocarb are expected to be low due to their more hydrophilic character; i.e., high water solubilities and low partition coefficients.

Although the literature affords no data regarding the persistence of benthiocarb, studies of other thiolcarbamate herbicides reported volatilization from field water as the major route of environmental dissipation (Soderquist et al., 1977; Cliath et al., 1980). Soderquist et al. (1977) found dilute aqueous solutions of molinate to be stable in sunlight. We had similar findings from our studies with benthiocarb. However, we found that the presence of sediment inhibited volatilization, as is evident from the high residues after 28 days in sterile sediment. Although benthiocarb is more persistent than other carbamates that we have studied, biotransformation in aquatic environments represents another major route in the pesticide's dissipation.

In contrast to the thiocarbamate herbicides, the literature is replete with data concerning the fate of organophosphate insecticides. Methyl parathion has been used by a number of investigators to calibrate processes in experimental systems or computer models for the purpose of predicting the environmental fate of chemicals (Baughman, 1980; Cole et al., 1977; Pritchard et al., 1979). Their data are similar to those we report for the persistence of methyl parathion, namely, rapid dissipation due to biotransformation in sediment or photolysis in sunlight. Freed et al. (1979) reported the half-life of chlorpyrifos in distilled water (53 days) and in moist Willamette soil (120 days). Pritchard (1981) reported a half-life of 19 days for chlorpyrifos in estuarine sediment–water microcosms. Although photolysis and hydrolysis are significant dissipative processes in our studies, chlorpyrifos, like the pyrethroids, rapidly partitions into bottom materials and suspended sediment where photolysis is hampered and biotransformation is slow. Other studies with artifical ponds have confirmed this hypothesis (Hughes et al., 1980).

In summary, our studies with benthiocarb, chlorpyrifos, and methyl parathion show that the acute toxicity values differed widely (benthiocarb LC_{50} values for invertebrates were 2 to nearly 4 orders of magnitude higher than those derived from exposure to chlorpyrifos and methyl parathion) and that their persistence (half-life) in seawater–sediment studies varied from 1.2 days (methyl parathion) to 24 days (chlorpyrifos). Chlorpyrifos may represent a potential hazard for benthic species due to its high acute toxicity and persistence in sediments.

Registry No. AC 222,705, 70124-77-5; fenvalerate, 51630-58-1; permethrin, 52645-53-1; chlorpyrifos, 2921-88-2; methyl parathion, 298-00-0; benthiocarb, 28249-77-6.

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